PERMEABILITY AND SELECTIVITY OF HYBRID MEMBRANE (PES/PSU) FOR GAS SEPARATION

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ABSTRACT

A hybrid membrane (PES/PSU) was prepared through a simple dry/wet phase inversion process. The casting solution developed in this research consists of PES, PSU, 1-methyl-2-pyrolidone (NMP) and methanol. Hybrid membrane (PES/PSU) is divided into three categories; uncoated, coated with polydimethylsiloxane (PDMS) and coated with bromine solution. Permeation test was carried out by testing CO_2, CH_4, N_2 and O_2 onto the hybrid membrane to see the permeability and selectivity of the respective gas to CH_4. Different coating agent gives different rate of permeate to the hybrid membrane. The hybrid membrane (PES/PSU) that coated with PDMS shows higher selectivity compared to conventional hybrid membrane and hybrid membrane that coated with bromine solution. The selectivity of CO_2/CH_4 is approximately 0.563, it is believed that different coating agent strongly affects the hybrid membrane performance.

ABSTRAK

Membran hibrid (PES/PSU) telah disediakan menggunakan teknik yang ringkas iaitu penyongsangan fasa basah/kering. Larutan bahan teracuan yang disediakan untuk kajian ini mengandungi PES, PSU, 1 metil 2 pyrolidone (NMP) dan metanol. Membran hibrid (PES/PSU) adalah dibahagi kepada tiga kategori; tidak ditutup, disalutkan dengan polidimetilsiloksana (PDMS) dan disalutkan dengan larutan bromin. Ujian penelapan telah dijalankan dengan menguji gas CO_2, CH_4, N_2 dan O_2 ke atas membran hibrid untuk melihat ketelapan dan pemilihan bagi setiap gas terhadap gas CH_4. Ejen salutan berbeza memberi nilai ketelapan yang berbeza kepada membrane hibrid. Membran hibrid yang bersalut dengan PDMS menunjukkan pemilihan lebih tinggi berbanding dengan membran hibrid konvensional dan membran hibrid yang bersalut dengan larutan bromin. Pemilihan bagi CO_2 / CH_4 adalah 0.563 dimana dipercayai bahawa ejen salutan mempengaruhi prestasi membran hibrid.

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CO_2	-	Carbon dioxide
PES	-	Polyethersulfone
PSU	-	Polysulfone
PDMS	-	Polydimethylsiloxane
NMP	-	N-Methyl-2-pyrrolidone
O_2	-	Oxygen
N_2	-	Nitrogen
H_2	-	Hydrogen
Cl	-	Chlorine
H_2S	-	Hydrogen sulfide
C_2	-	Carbon
J	-	Flowrate of gas through membrane
ℓ	-	The effective thickness of separation layer
D	-	Diffusion coefficient in membrane
ΔC	-	Concentration difference of gas in membrane
S	-	Solubility coefficient
P	-	External gas partial pressure
P/ℓ	-	Gas permeance
P	-	Permeability coefficient of separation layer
A	-	Membrane surface area
Δp	-	Pressure difference of penetrant across membrane
α	-	Selectivity of gas
SEM	-	Scannin Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural gas is a gaseous fossil fuel consisting primarily of methane but including significant quantities of ethane, propane, butane, and as well as carbon dioxide, nitrogen, helium and hydrogen sulfide. It is found in oil fields either dissolved or isolated in natural gas fields, and in coal beds. When methane-rich gases are produced by the anaerobic decay of non-fossil organic material, these are referred to as biogas. Sources of biogas include swamps, marshes and landfills as well as sewage sludge and manure by way of anaerobic digesters, in addition to enteric fermentation particularly in cattle (Rojey A. *et al.*, 1997).

In separation of gases, membranes offer the greatest potential. In interaction with a membrane, a high degree of permeability coupled with a large selectivity of a specific gaseous species ensures superior performances in the gas processing industry. Economically, the advantage of membrane separation technology is immense. The separation of natural gas by thin barriers termed as membranes is a dynamic and rapidly growing field, and it has been proven to be technically and economically superior to other emerging technologies. This superiority is due to certain advantages which membrane technology benefits from, including low capital investment, low weight, and space requirement and high process flexibility (Kohl *et al.*, 1997). In the past ten years the membrane gas separation technology has advanced greatly and can now be regarded as a competitive industrial gas separation method.

A high permeability and selectivity can be achieved by conducting a permeation test towards the gases. However, in the reality, a high permeability contributes to low selectivity and vice versa. Therefore, we can't expect the excellent result but we can improve the selectivity if it gives the high permeability. One method of improving it is by using the method of coating the membrane. Coating may lessen the defect skin layers which happen in the structure of membrane.

1.2 Problem Statement

Carbon dioxide (CO_2) which falls into the category of acid gas is commonly found in natural gas streams at levels as high as 80%. In combination with water, it is highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed or exotic and expensive construction materials are used. Carbon dioxide also reduces the heating value of a natural gas stream and wastes pipeline capacity. In LNG plants, CO_2 must be removed to prevent freezing in the low-temperature chillers (Tobin J., 2006).

A wide variety of acid gas removal technologies are available. They include absorption processes; cryogenic processes; adsorption processes; and membranes. Each process has its own advantages and disadvantages, but membranes increasingly are being selected for newer projects, especially for applications that have large flows, have high CO_2 contents, or are in remote locations.

Membranes have been widely used in two main CO_2 removal applications:

- Natural gas sweetening
- Enhanced oil recovery (EOR), where CO_2 is removed from an associated natural gas stream and reinjected into the oil well to enhance oil recovery

However the major problems confronting the use of the membrane based gas separation processes in a wide range of applications is the lack of membranes with high permeability and high selectivity. Therefore, a membrane which has high permeability and also not depleting in the level of selectivity is sought off in order to overcome this problem.

1.3 Objective of Study

The objective of this research is to study the permeability and selectivity Hybrid membrane (PES/PSU) using gases (N_2, CO_2, CH_4 and O_2) and to study the performance of Hybrid membrane treatment using coating and uncoating method.

1.4 Scope of Study

The scopes which need to be focused in order to meet the objective are:

i. Develop and study the permeability and selectivity of the Hybrid membrane (PES/PSU) for gas separation
ii. Study the effect of Hybrid membrane permeability and selectivity by coating and uncoating in order to reduce the defect skin layers.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Gas

Natural gas is a mixture of hydrocarbons, predominantly methane (CH_4). Most natural gas is extracted from gas and oil wells. Much smaller amounts are derived from supplemental sources such as synthetic gas, landfill gas and other biogas resources, and coal-derived gas. Natural gas that comes from oil wells is typically termed 'associated gas'. This gas can exist separate from oil in the formation (free gas), or dissolved in the crude oil (dissolved gas). Natural gas from gas and condensate wells, in which there is little or no crude oil, is termed 'non-associated gas'. Gas wells typically produce raw natural gas by itself, while condensate wells produce free natural gas along with a semi-liquid hydrocarbon condensate (Rojey A. *et al.,* 1997).

Natural Gas that has been processed is a gaseous fossil fuel consisting primarily of methane and including significant quantities of ethane, propane, butane, and pentane. It did not contain heavier hydrocarbons because they were removed prior to use as a consumer fuel as well as carbon dioxide, nitrogen, helium and hydrogen sulfide. It is found in oil fields (associated) either dissolved or isolated in natural gas fields (non-associated), and in coal beds (as coalbed methane). When methane-rich gases are produced by the anaerobic decay of non-fossil organic material, these are referred to as biogas.

Sources of biogas include swamps, marshes, and landfills (see landfill gas), as well as sewage sludge and manure by way of anaerobic digesters, in addition to enteric fermentation particularly in cattle.

2.2 Membrane Separation Process

Membrane separation processes have emerged during the last two decade as a promising alternative to some conventional separation processes and offer a number of important advantages for upgrading of crude natural gas. Essentially, a membrane can be defined as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. A membrane separation system separates an influent stream into two effluent streams known as the permeate and the concentrate. The permeate is the portion of the fluid that has passed through the semi-permeable membrane while the other is the gas concentrated flow out the reject steam.

Membrane separation process enjoys numerous industrial applications with the following advantages (Kohl *et al.*, 1997):

- Appreciable energy savings
- Environmentally benign
- Clean technology with operational ease
- Replaces the conventional processes like filtration, distillation, ion-exchange and chemical treatment systems
- Produces high, quality products
- Greater flexibility in designing systems.

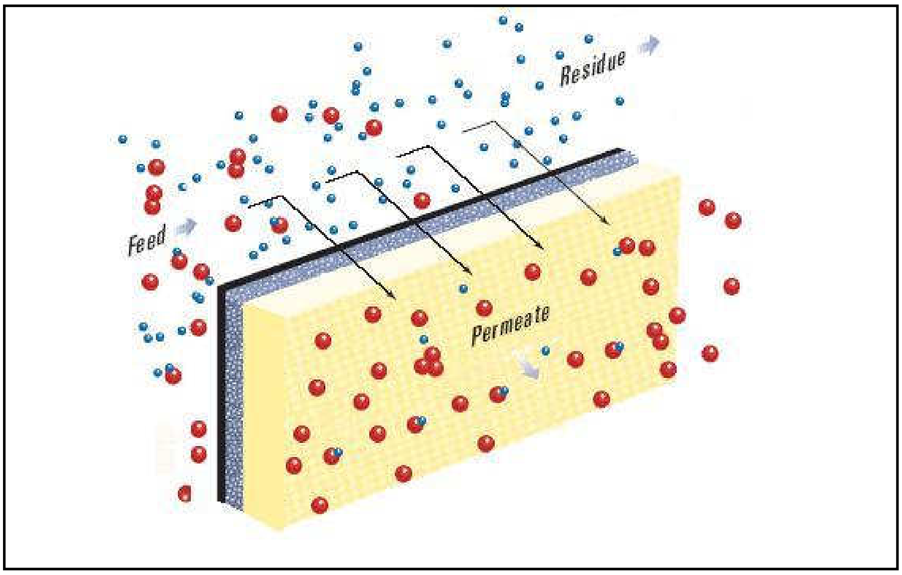

Figure 2.1: Schematic diagram of membrane separation process

Figure 2.1 show the mechanism of the transport of gases through nonporous membranes involves the following action (Kohl *et al.*, 1997):

- adsorption of the gas at one surface of the membrane,
- solution of the gas into the membrane,
- diffusion of the gas through the membrane,
- release of the gas from solution at the opposite surface, and
- desorption of the gas from the surface (permeate).

2.3 Type of Membrane Separation Process

Currently, there are seven type of membrane separation process which are reverse osmosis, nanofiltration, ultrafiltration, microfiltration, electrodialysis, gas permeation in a membrane and pervaporation. This membrane separation process is classified based on pore size (Srikanth G., 1999).

2.3.1 Reverse Osmosis (RO)

Reverse Osmosis (RO) is a pressure driven membrane diffusion process for separating dissolved solutes. The RO is generally used for desalination seawater for its conversion into potable water. The salient features of the process are that it involves no phase change and it is relatively a low energy process. Compared to water filtration, which can only remove some suspended materials larger than 1 micron, the process of RO will eliminate the dissolved solids, bacteria, viruses and other germs contained in the water. Almost all RO membranes are made polymers, cellulose acetate and matic polyamide types rated at 96% to 99% NaCl rejection. RO membranes are generally of two types, asymmetric or skinned membranes and thin film composite (TFC) membranes. The support material is commonly polysulfones while the thin film is made from various types of polyamines, polyureas etc.

RO membranes have the smallest pore structure, with pore diameter ranging from approximately 5-15 A^0 (0.5 nm - 1.5 nm). The extremely small size of RO pores allows only the smallest organic molecules and unchanged solutes to pass through the semi-permeable membrane along with the water. Greater than 95-99% of inorganic salts and charged organics will also be rejected by the membrane due to charge repulsion established at the membrane surface. Figure 2.2 shows the schematic diagram of reverse osmosis (Srikanth G., 1999).

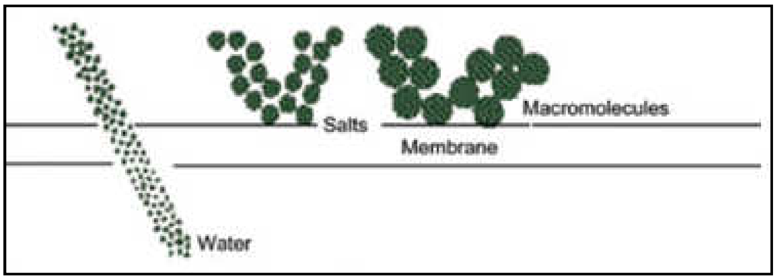

Figure 2.2: Reverse osmosis membrane process

2.3.2 Nanofiltration (NF)

Nanofiltration (NF) is a form of filtration that uses membranes to separate different fluids or ions. NF is typically referred to as "loose" RO due to its larger membrane pore structure as compared to the membranes used in RO, and allows more salt passage through the membrane. Because it can operate at much lower pressures, and passes some of the inorganic salts, NF is used in applications where high organic removal and moderate inorganic removals are desired. NF is capable of concentrating sugars, divalent salts, bacteria, proteins, particles, dyes and other constituents that have a molecular weight greater than 1000 daltons.

Membranes used for NF are of cellulosic acetate and aromatic polyamide type having characteristics as salt rejections from 95% for divalent salts to 40% for monovalent salts and an approximate 300 molecular weight cut-off (MWCO) for organics. An advantage of NF over RO is that NF can typically operate at higher recoveries, thereby conserving total water usage due to a lower concentrate stream flow rate. NF is not effective on small molecular weight organics, such as methanol (Srikanth G., 1999). Figure 2.3 shows the schematic diagram of nanofiltration process.

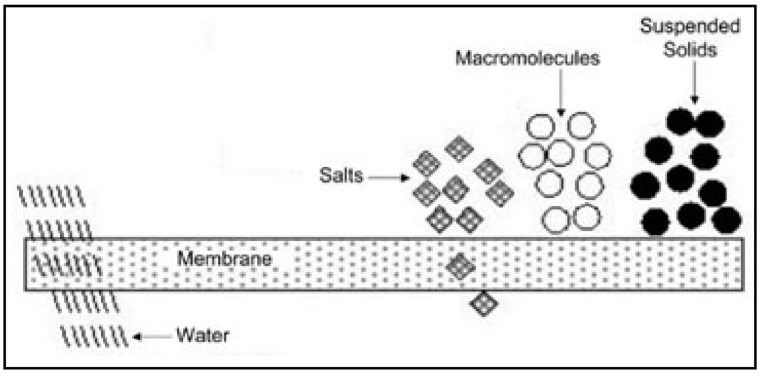

Figure 2.3: Nanofiltration membrane process.

2.3.3 Ultrafiltration (UF)

Ultrafiltration (UF) is used to separate a solution that has a mixture of some desirable components and some that are not desirable. UF is somewhat dependent on charge of the particle, and is much more concerned with the size of the particle. Typical rejected species include sugars, bio-molecules, polymers and colloidal particles. The driving force for transport across the membrane is a pressure differential. UF processes operate at 2-10 bars though in some cases up to 25-30 bars have been used. UF processes perform feed clarification, concentration of rejected solutes and fractionation of solutes. UF is typically not effective at separating organic streams.

UF membranes are capable of retaining species in the range of 300-500,000 daltons of molecular weight, with pore sizes ranging from 10-1000 Angstroms (10^3-0.1 microns). These are mostly described by their nominal molecular weight cutoff (1000-100,000 MWCO), which means, the smallest molecular weight species for which the membranes have more than 90% rejection (Srikanth G., 1999). Figure 2.4 shows the schematic diagram of ultrafiltration process.

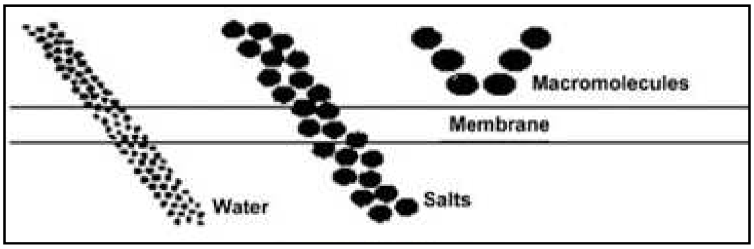

Figure 2.4: Ultrafiltration membrane process.

2.3.4 Microfiltration (MF)

Microfiltration (MF) is a process of separating material of colloidal size and larger than true solutions. A MF membrane is generally porous enough to pass molecules of true solutions, even if they are large. Microfilters can also be used to sterilize solutions, as they are prepared with pores smaller than 0.3 microns, the diameter of the smallest bacterium, *pseudomonas diminuta*. It is essentially a sterile filtration with pores (0.1-10.0 microns) so small that micro-organisms cannot pass through them.

MF membranes use *sieving mechanism* with distinct pore sizes for retaining larger size particles than the pore diameter. Hence, this technology offers membranes with absolute rating, which is highly desirable for critical operations such as sterile filtration of parental fluids, sterile filtration of air and preparation of particulate, free-water for the electronics industry.

The MF membranes are made from natural or synthetic polymers such as cellulose nitrate or acetate, polyvinylidene difluoride (PVDF), polyamides, polysulfone, polycarbonate, polypropylene, PTFE etc. The inorganic materials such as metal oxides (alumina), glass, zirconia coated carbon etc. are also used for manufacturing the microfiltration membranes (Srikanth G., 1999). Figure 2.5 shows the schematic diagram of microfiltration process.

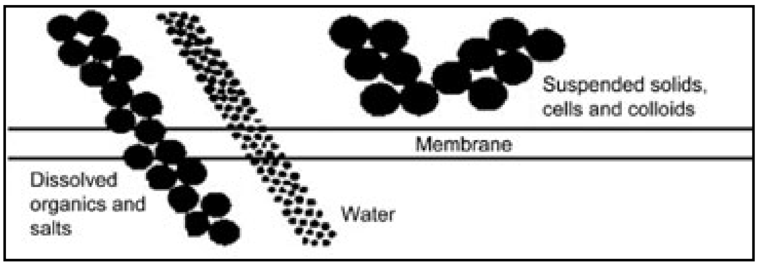

Figure 2.5: Microfiltration membrane process.

2.3.5 Electrodialysis (ED)

Electrodialysis (ED) is an electro-membrane process in which the ions are transported through a membrane from one solution to another under the influence of an electrical potential. ED can be utilized to perform several general types of separations such as separation and concentration of salts, acids and bases from aqueous solutions or the separation and concentration of monovalent ions from multiple charged components or the separation of ionic compounds from uncharged molecules. ED membranes are usually made of cross-linked polystyrene that has been sulfonated. Anion membranes can be of cross-linked polystyrene containing quaternary ammoniuri groups. Usually, ED membranes arx fabricated as flat sheets containing about 30-50% water. Membranes are fabricated by applying the cation and anion-selective polymer to a fabric material.

The system consists of two kinds of membranes: cation and anion, which are placed in an electric field. The cation-selective membrane permits only the cations and anion-selective membrane only the anions. The transport of ions across the membranes results in ion depiction in some cells, and ion concentration in alternate ones. ED is used widely for production of potable water from sea or brackish water, electroplating rinse recovery, desalting of cheese whey, and production of ultrapure water (Srikanth G., 1999).

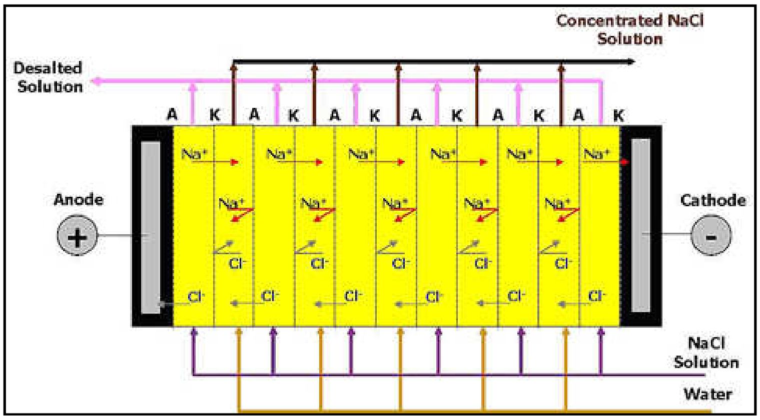

Figure 2.6: Electrodialysis membrane process

2.3.6 Gas Permeation in a Membrane

The membrane processes give certain advantages such as compactness and light in weight, low labour intensity, modular design permitting easy expansion or operation at partial capacity, low maintenance (no moving parts), low energy requirements and low cost especially so for small sizes. Membranes made of polymers and copolymers in the forms of flat film or hollow fiber have been used for gas separation.

Different gases pass through certain membranes at significantly different rates, thus permitting a partial separation. The rate of permeation is proportional to the pressure differential across die membrane and inversely proportional to the membrane thickness. The rate of permeation is also proportional to the solubility of the gas in the membrane and also to the diffusivity of gas through the membrane. Figure 2.7 show the gas permeation process.

Gas separation is thus affected by three key performance attributes of membranes that is selectivity towards the gases separated, membrane flux or permeability and the life of the membrane, maintenance and replacement costs.

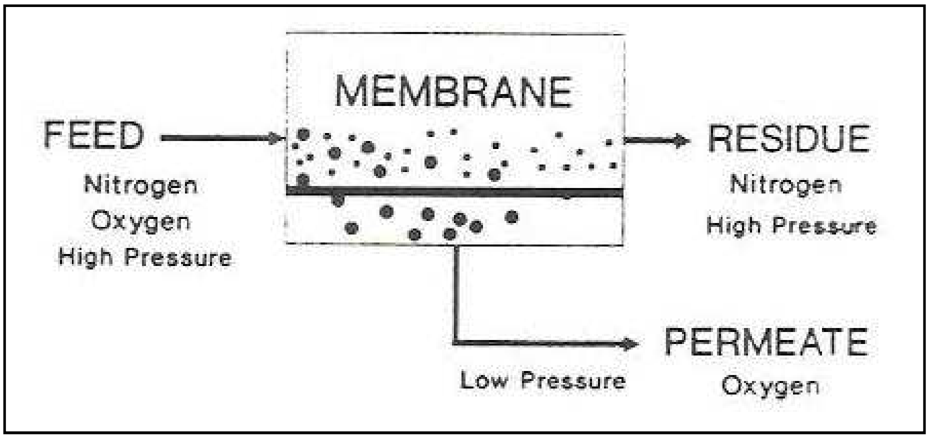

Figure 2.7: Gas permeation membrane process

2.3.7 Pervaporation

Pervaporation is a membrane based process for separating miscible liquids. The absorption of one of the components of the liquid by the membrane, diffusion of this component across the membrane and evaporation, as permeate vapour, into the partial vacuum applied to the underside of the membrane. Pervaporation differs from all other membrane processes because of the phase change of the permeate, non-porous. Transport through these membranes is affected by maintaining a vapour pressure gradient across the membrane. Pervaporation has been used for separation of ethanol-water mixture, solvent recovery, separation of heat sensitive products or enrichment of organic pollutants etc. (Mulder, 1996).

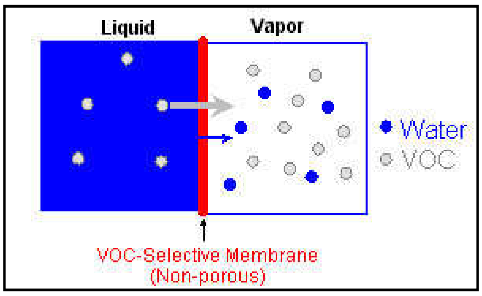

Figure 2.8: Pervaporation membrane process

2.4 Membrane Type and Application

Membranes can be generally classified into three groups which is artificial membrane, polymeric and semipermeable membrane. These three types of membranes differ significantly in their structure and functionality.